

10/612,850

PTO 07-6780

CC = JP
19890307
Kokai
64060679

JP 64-60679

ADHESIVE COMPOSITIONS FOR STICKING ELECTRONIC PARTS
[Setchakuzaiseibutsu]

Yoshiaki Murakami et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. SEPTEMBER 2007
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	6460679
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	19890307
APPLICATION NUMBER	(21):	62216116
APPLICATION DATE	(22):	19870828
INTERNATIONAL CLASSIFICATION ⁴	(51):	C 09 J 3/16 H 01 L 21/60 H 05 K 3/34
INVENTORS	(72):	Yoshiaki Murakami et al.
APPLICANTS	(71):	Shinko Kagaku Kogyo K.K.
TITLE	(54):	ADHESIVE COMPOSITIONS FOR STICKING ELECTRONIC PARTS
FOREIGN TITLE	[54A]:	Setchakuzaisoseibutsu

Claim

Adhesive compositions for sticking electronic parts, characterized in that the adhesive compositions comprise the following components [A]-[D];

[A] epoxy resin having an epoxy equivalent of 250-1200 g/eq and obtained by mixing one or more of bisphenol A type epoxy resin, ortho-cresol novolak type epoxy resin, polyphenol type epoxy resin and reaction product between butadiene-acrylonitrile copolymer having carboxyl group at both ends and epoxy resin,

[B] acrylonitrile copolymer containing carboxyl group,

[C] tertiary amines or imidazole compounds, and

[D] hardening agents for epoxy resin, and

as the content of each component per 100 parts by weight of epoxy resin of [A], the acrylonitrile copolymer of [B] is 50-300 parts by weight, and the tertiary amines or imidazole compounds of [C] is 0.5-5.0 parts by weight.

Detailed explanation of the invention

Industrial application field

The present invention relates to adhesive compositions for sticking electronic parts, which are used for the formation of adhesive layers (adhesion films) for sticking tape-form or film-form flexible insulation films (flexible carrier films or the like) to electronic parts or sticking metallic conductors to other objects.

* [Numbers in right margin indicate pagination of the original text.]

Prior art

In adhesives for sticking electronic parts such as carrier tapes, printed circuits or the like, the adhesion property between insulation substrates and electronic parts, heat resistance to solder, electric property, chemical resistance, dimensional stability, and the like are required.

Adhesive films have been disclosed (Kokai Patent Sho 55[1980]-63857), which are obtained by mixing, as the adhesives, copolymerized nylon-modified epoxy resin system adhesives, phenol butyral system adhesives, modified polyester system adhesives, acrylic system adhesives or nitrile rubber-modified epoxy resin system adhesives with at least 3% by weight of inorganic fillers.

/2

Problem to be solved by the invention

However, these adhesive films have the following drawbacks and their application range is restricted.

Namely, in the case where the thickness of insulation substrates is less than 75 μm , if the adhesive films are thermally hardened, the films are curled so that high-accuracy circuit patterns can not be formed since the tensile elastic modulus of the hardened films is high.

Further, in the aforementioned adhesive films formed by using copolymerized nylon-modified epoxy resin system adhesives, the copolymerized nylon as a component sometimes contaminates the plating solutions in addition so that the films become easily hygroscopic and are inferior in the heat resistance to solder.

Furthermore, phenol butyral system adhesives and polyester system adhesives become easily hygroscopic and are inferior in the heat resistance to solder, whereas acrylic system adhesives and nitrile rubber-modified epoxy system adhesives are inferior in the adhesion property.

Means to solve the problems

As a result of intensive research and investigation made by the present inventors on the aforementioned problems, it has been found that adhesive compositions obtained by mixing epoxy resin, acrylonitrile copolymer, tertiary amines or imidazole compounds, and epoxy resin hardening agents at a specified mixing ratio are extremely superior in the adhesion property and heat resistance to solder, and the present invention has been accomplished by the aforesaid finding and information.

That is, the adhesive compositions for sticking electronic parts by the present invention are characterized in that the adhesive compositions comprise the following components [A]-[D];

[A] epoxy resin having an epoxy equivalent of 250-1200 g/eq and obtained by mixing one or more of bisphenol A type epoxy resin, ortho-cresol novolak type epoxy resin, polyphenol type epoxy resin and reaction product between butadiene-acrylonitrile copolymer having carboxyl group at both ends and epoxy resin,

[B] acrylonitrile copolymer having carboxyl group,

[C] tertiary amines or imidazole compounds, and

[D] hardening agents for epoxy resin, and

as the content of each component per 100 parts by weight of epoxy resin of [A], the acrylonitrile copolymer of [B] is 50-300 parts by weight, and the tertiary amines or imidazole compounds of [C] is 0.5-5.0 parts by weight.

Hereinafter, the present invention is explained in detail.

As epoxy resin to be used in the present invention, epoxy resin having an epoxy equivalent of 250-1200 g/eq and obtained by mixing one or more of bisphenol A type epoxy resin, ortho-cresol novolak type epoxy resin, polyphenol type epoxy resin and reaction product between butadiene-acrylonitrile copolymer having carboxyl group at both ends and epoxy resin is exemplified.

As the aforementioned bisphenol A type epoxy resin [A], those having an epoxy equivalent of 180-1200 g/eq are exemplified, and there are Epikote 328, Epikote 111001 (produced by Yuka Shell Epoxy Co., Ltd.), DER542 (both produced by Dow Chemical Co., Ltd.), and the like as articles on the market.

As the aforementioned ortho-cresol novolak type epoxy resin, those having an epoxy equivalent of 190-230 g/eq are exemplified, and there are Sumiepoxy ESCN-195xHH, Sumiepoxy ESCN-220HH (both produced by Sumitomo Chemical Industry Co., Ltd.), and the like as articles on the market.

As the aforementioned polyphenol type epoxy resin, those having an epoxy equivalent of 200-220 g/eq are exemplified, and there are Epikote 11031 (produced by Yuka Shell Epoxy Co., Ltd.) and the like as articles on the market.

- 11 Further, as reaction products between butadiene-acrylonitrile copolymer having carboxyl group at both ends and epoxy resin, those having an epoxy equivalent of 500-1500 g/eq are exemplified, and
13 there are Epomic SR-35 (produced by Mitsui Petrochemical Co., Ltd.), etc. as articles on the market.

In the present invention, epoxy resin having an epoxy equivalent of 250-1200 g/eq selected from the above-mentioned epoxy resins singly or in combination of two or more is used. /3

When the epoxy equivalent is less than 250 g/eq, hardened materials from adhesive compositions become fragile and the adhesive strength lowers. On the other hand, when the epoxy equivalent exceeds 1200 g/eq, the compatibility with acrylonitrile copolymer having carboxyl group at solution state is deteriorated and homogeneous compositions can not be obtained.

Further, acrylonitrile copolymer having carboxyl group [B] to be used in the present invention is NBR having an acrylonitrile content of 20-50% by weight and a carboxyl group content, as hydroxyl value, of 1-100 KOH mg/g, and there are Nipol 1072 (produced by Nippon Zeon Co., Ltd.) and the like as articles on the market.

The mixing amount of [B] is preferably 50-300 parts by weight per 100 parts by weight of the aforementioned epoxy resin [A]. If the mixing amount is less than 50 parts by weight, the thickness of insulation films having tensile elastic modulus of 1000 kg/mm^2 or less becomes $25 \text{ }\mu\text{m}$ or higher and curling occurs since the tensile elastic modulus of hardened materials exceeds 75 kg/mm^2 . On the other hand, if it exceeds 300 parts by weight, the chemical resistance lowers.

Furthermore, as tertiary amines or imidazole compounds [C] to be used in the present invention, those, which have been used as polymerization catalysts of epoxy group or hardening accelerator of epoxy resins, may be used without any restriction, and concrete examples of [C] include benzyldimethylamine, 2,4,6-tris(dimethylaminomethyl)phenol, 2-ethyl-4-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, and the like.

When [C] is added at an amount of 0.5-5.0 parts by weight per 100 parts by weight of the epoxy resin [A], it reacts at solution state with acrylonitrile copolymer containing carboxyl group to raise the melt viscosity so that the adhesive strength of those adhered using the composition is notably enhanced as compared with that from compositions containing neither tertiary amines nor imidazole compounds.

When the mixing amount of [C] is less than 0.5 part by weight, its effect does not arise whereas when it exceeds 5.0 parts by weight the wettability of the adhesives lowers or the preservability at prepreg state is deteriorated.

Furthermore, as epoxy resin hardening agents [D] to be used in the present invention, ordinary hardening agents for epoxy resins are used without any restriction, and examples of the hardening agents include glyoxal, acid anhydrides, various amines, isocyanate compounds, polyester amide resins, imidazole compounds, dicyandiamide, trifluoride complex of amine, and the like.

The mixing ratio of [D] is largely varied with type of [D], but the amount sufficient for hardening the aforementioned epoxy resin is satisfactorily used.

The adhesive compositions for sticking electronic parts of the present invention comprise 100 parts by weight of epoxy resin of [A], 50-300 parts by weight of acrylonitrile copolymer of [B], 0.5-5.0 parts by weight of tertiary amines or imidazole compounds of [C], and epoxy resin hardening agents of [D].

In general, the adhesive compositions for sticking electronic parts of the present invention are diluted in solvents and coated on coating objects.

Publicly known solvents are used as the solvent, and examples of these solvents include ketone system solvents, ether system solvents, and chlorinated hydrocarbon system solvents. These solvents can be used singly or in combination of two or more.

Examples of the aforementioned ketone system solvents include methyl ethyl ketone, methyl isobutyl ketone, and the like. Examples of the aforementioned ether type solvent include dioxane, methyl cellosolve, dimethyl cellosolve, and the like. Furthermore, examples of the aforementioned chlorinated hydrocarbon system solvents include methylene chloride, ethylene chloride, carbon tetrachloride, trichloroethylene, and the like.

Action

The present invention has the aforestated constitution, and the epoxy resins to be used in the present invention improve the heat resistance and chemical resistance of hardened materials from the adhesive compositions, and the acrylonitrile copolymer actualizes (P.562) stress relaxation of adhesion peeling forces and lowering of elastic modulus of hardened materials from the adhesive compositions.

Furthermore, the tertiary amines or imidazole compounds improve the adhesive strength. After all, those coupled with each other have action for improving various properties such as adhesion property, heat resistance to solder, electric properties and the like.

Application examples

Hereinafter, the present invention is explained in detail based on application examples, but the present invention is not limited to these.

Application Example 1

A composition comprising 50 parts by weight of bisphenol A type epoxy resin (Epikote 828, epoxy equivalent 130 g/eq, produced by Yuka Shell Epoxy Co., Ltd.) as epoxy resin [A], 50 parts by weight of bisphenol A type epoxy resin (Epikote 1001, epoxy equivalent 475 g/eq, produced by Yuka Shell Epoxy Co., Ltd.) also as epoxy resin [A], 150 parts by weight of Nipol 1072 (trade name) produced by Nippon Zeon Co., Ltd. as carboxyl group-containing acrylonitrile copolymer [B], 1.5 parts by weight benzyldimethylamine as tertiary amine [C], and 26.0 parts by weight of 4,4'-diaminodiphenylsulfone as epoxy resin hardening agent [D] was dissolved in 500 parts by weight of methyl ethyl ketone to obtain a homogeneous solution.

Application Examples 2-5

Adhesive solutions of application examples 2-5 were prepared from adhesive compositions shown in Table 1 by the same method as that in Application Example 1.

Reference Examples 1-5

Adhesive solutions of reference examples 1-5 were prepared from adhesive compositions shown in Table 2 by the same method as that in Application Example 1.

Comparative Example 1

An adhesive containing 10% by weight (based on base adhesive excluding solvent), based on copolymerized nylon/epoxy system as base adhesive, of silica as an inorganic powder was used.

Comparative Examples 2-5

Adhesives, which were the same adhesives as that in Comparative Example 1 except that calcium carbonate (comparative example 2), silica/magnesium oxide (weight ratio 2/1) (comparative example 3), titanium oxide (comparative example 4) and alumina (comparative example 5), instead of silica, were used as inorganic powder, were used.

Table 1

Material name		Application Example 1	Application Example 2	Application Example 3	Application Example 4	Application Example 5
Epoxy resin	a	50	50	50	50	50
	b	50				
	c		50			
	d			50		
	e				50	
	f					50
Acrylonitrile copolymer	g	150	150	200	250	100
Tertiary amine	h	1.5				
	i		2.0			
Imidazole compound	j			2.5		
	k				3.0	3.5
Epoxy resin hardener	l	26		36	36	
	m		4			4

Table 2

/5

Material name		Reference Example 1	Reference Example 2	Reference Example 3	Reference Example 4	Reference Example 5
Epoxy resin	a	50	100	50	50	50
	b	50				
	c					
	d			50		
	e				50	
	f					50
Acrylonitrile copolymer	g	150	150	350	30	100
Tertiary amine	h					
	i		2.0			
Imidazole compound	j			2.5		
	k				3.0	7.0
Epoxy resin hardener	l	26		36	36	
	m		4			4

- a: bisphenol A type epoxy resin (Epikote 828, epoxy equivalent 190 g/eq, produced by Yuka Shell Epoxy Co., Ltd.)
- b: bisphenol A type epoxy resin (Epikote 1001, epoxy equivalent 475 g/eq, produced by Yuka Shell Epoxy Co., Ltd.)
- c: borominated bisphenol A type epoxy resin (DER 542, epoxy equivalent 375 g/eq, produced by Dow Chemical Co., Ltd.)
- d: ortho-cresol novolak type epoxy resin (Sumiepoxy EGCN-220 HH, epoxy equivalent 205 g/eq, produced by Sumitomo Chemical Industry Co., Ltd.)
- e: polyphenol type epoxy resin (Epikote 1031, epoxy equivalent 210

g/eq, produced by Yuka Shell Epoxy Co., Ltd.)

f: reaction product between butadiene-acrylonitrile copolymer and epoxy

resin (Epomic SR-35, epoxy equivalent 985 g/eq, Mitsui Petrochemical Co., Ltd.)

g: carboxyl group-containing acrylonitrile copolymer (Nipol 1072,

acrylonitrile content 27%, produced by Nippon Zeon Co., Ltd.)

h: benzyldimethylamine

i: 2,4,6-tris(dimethylaminomethyl)phenol

j: 2-ethyl-4-methylimidazole

k: 1-cyanoethyl-2-ethyl-4-methylimidazole

l: 4,4'-diaminodiphenyl sulfone

m: dicyandiamide

The results of various property tests for the aforementioned application examples, comparative examples and reference examples are given in Table 3, Table 4, and Table 5, respectively.

Table 3

Items	Application Example 1	Application Example 2	Application Example 3	Application Example 4	Application Example 5
Adhesion hardening condition (note 1)	a	b	a	b	a
Adhesive strength kg/cm (note 2)	2.1	2.0	2.2	2.3	2.0
Tensile elastic modulus kg/cm ² (note 3)	34	42	30	28	60
Occurrence of curling (note 4)	O	O	O	O	O
Heat resistance to solder	120 or	120 or	120 or	120 or	120 or

second, (note 5)	higher	higher	higher	higher	higher
Chemical resistance (note 6)	O	O	O	O	O

Table 4

/6

Items	Application Example 1	Application Example 2	Application Example 3	Application Example 4	Application Example 5
Adhesion hardening condition (note 1)	a	b	a	b	a
Adhesive strength kg/cm (note 2)	2.2	2.1	2.1	2.0	2.0
Tensile elastic modulus kg/cm ² (note 3)	88	86	82	85	90
Occurrence of curling (note 4)	X	X	X	X	X
Heat resistance to solder second, (note 5)	10 or less	12 or less	8 or less	2 or less	3 or less
Chemical resistance (note 6)	O	O	O	O	O

Table 5

Items	Reference Example 1	Reference Example 2	Reference Example 3	Reference Example 4	Reference Example 5
Adhesion hardening condition (note 1)	a	b	a	b	a
Adhesive strength kg/cm (note 2)	1.1	0.8	1.6	0.7	0.4
Tensile elastic modulus kg/cm ² (note 3)	34	170	25	265	62
Occurrence of curling (note 4)	O	X	O	X	O
Heat resistance to solder	60	60	12	60	5

second, (note 5)					
Chemical resistance (note 6)	O	O	X	O	O

(Note 1) Adhesion hardening condition

Capton 200H (polyimide film, thickness 50 μm , produced by Du Pont-Toray Co., Ltd.) as a flexible film was adhered to a 35 μm -thick electrolytic copper foil as a metallic conductor under the condition shown below using 20 μm -thick adhesive compositions (films) of application examples shown in Table 1, comparative examples, and reference examples shown in Table 2.

[a] Lamination hardening was carried out as follows. As lamination condition, preheating at 150-160°C for 1-2 min, roll temperature 100-120°C, pressure 2-4 kg/cm^2 ; as post curing condition, at 60°C for 6 h in the first stage, at 80°C for 3 h in the second stage, at 110°C for 6 h in the third stage, and at 150°C for 6 h in the fourth stage.

[b] Adhesion hardening was carried out as follows. As press adhesion condition, at 180°C and pressure 75 kg/cm^2 for pressing time of 60 min; and as post curing condition, at 190°C for 60 min.

(Note 2) Adhesive strength

On samples adhered under the condition of (note 1), 180 degree peeling strength of copper foil at a peeling rate of 50 mm/min was measured.

(Note 3) Tensile elastic modulus

On a sample obtained by hardening a 20 μm -thick adhesion composition (film) under the condition of (note 1), the tensile elastic modulus was measured at a tensile velocity of 4 mm/minute using tensile testing machine Tensilon of Toyo Baldwin Co., Ltd.

(Note 4) Occurrence of curling

On a sample adhered under the condition of (note 1), the occurrence state of curling was observed.

Evaluation: O no curling
 X occurrence of curling

(Note 5) Heat resistance to solder

On a sample adhered under the condition of (note 1), it was floated by placing the flexible film at top side on molten solder kept at $300\pm 5^{\circ}\text{C}$ and the time until abnormality occurred in the sample was measured.

(Note 6) Chemical resistance

On a sample adhered under the condition of (note 1), the copper foil was removed by etching, and after dipping it in 1,1,1-trichloroethane at normal temperature for 24 h the change of adhesive layer was observed.

Evaluation: O no change
 X there is a change such as swelling, etc.

17

As is clear from Table 3, it is confirmed that the adhesive compositions of the present invention are superior in heat resistance and chemical resistance and have no curling due to high adhesive strength and low elastic modulus so that circuit patterns can be obtained at high accuracy even in flexible films having a thickness less than $75\text{ }\mu\text{m}$.

In contrast to this, it is confirmed in those of comparative examples that curling easily occurs since elastic modulus is high and all of those are inferior in heat resistance to solder since copolymerized nylon gets easily moisten as it is seen in Table 4.

Further, it is conformed from Table 5 that in adhesive compositions shown in reference examples, not only sufficient adhesive strength, heat resistance and chemical resistance can not be obtained but also curling easily occurs so that it is difficult to form circuit patterns at high accuracy.

Effect of the invention

The present invention has the aforestated constitution and uses specific epoxy resin as the main component in the adhesive compositions so that the adhesive strength can be raised under retaining of heat resistance and chemical resistance. Further the elastic modulus of the thermally hardened materials from said adhesive compositions is lowered and curling does not occur by adding a specified amount of acrylonitrile copolymer so that circuit patterns of high accuracy can not be obtained. Furthermore, the adhesive strength is notably improved by addition of tertiary amines or imidazole compounds.